Impedance of Corrosion Related Electrode Processes. New Insight in the Origin of the Time-constants from Coupling Effects with the Double-Layer

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Electrochemical Impedance Spectroscopy (EIS) has become a widely used technique for investigating the complex processes at solid electrodes in many important fields particularly corrosion. Interpretation of EIS data remains a key-point for its practical use for both mechanistic and practical purposes, like corrosion rate evaluation. Most interpretations of the low frequency time-constants rely on kinetics models which involve the relaxation of potential dependent parameters related to interfacial phases, either 2-d (coverage by adsorbed intermediate) or 3-d (thickness of passive layers).

1. Background

It is generally assumed that the double layer structure is not affected by these surface processes even though capacitance measurements were applied to the inhibition by organic molecules or to semiconductor description of the passive films. This keynote is aimed at presenting an original approach based on the modulation of the double layer by the corrosion related processes. The principle and experimental equipment were described previously [1, 2]. The information are entirely contained in a new transfer function, DLCFR: $\Delta C_\Omega(\omega)/\Delta E\omega$ (unit F V^{-1} cm^{-2}) displaying the Frequency Response of the Double Layer Capacitance sampled at Ω ($\geq$1kHz) when the electrode impedance is measured simultaneously at a lower frequency ω.

2. Results and discussion

Results reported will deal with open-circuit corrosion, anodic dissolution in the active range, passivation, passivity and transpassivity of iron or nickel.

Anodic dissolution of iron in acidic media

Figure 1 displays the electrode admittance and Figure 2 $\Delta C_\Omega(\omega)/\Delta E_\omega$ measured simultaneously.
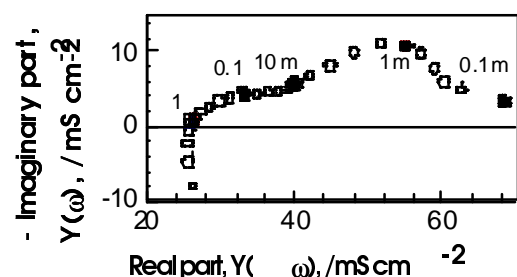

Figure 1: complex plane plot of admittance of Fe in1M Na$_2$SO$_4$ acidified to pH 4. Rotation speed:600 rpm
$I = 0.51$ mA cm^{-2}. $\Delta E_\omega = 10$mV rms.Frequency in Hz
Both transfer functions exhibit two inductive-like loops [3] in the upper part of the complex plane (negative

imaginary part) with alike frequency ranges and relative sizes. The observed phenomenon may be interpreted by an interaction of the flux of cations with the double layer properties as expected from [4, 5]. However classical equilibrium models assuming a modification of the double layer capacitance by the interfacial species can be applied.
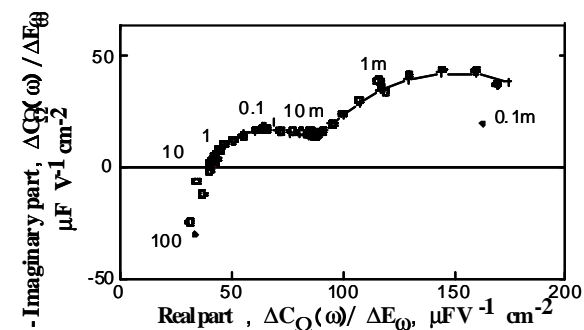

Figure 2 : complex plane plot of DLCFR: $\Delta C_\Omega(\omega)/\Delta E_\omega$. Same conditions as for Figure 1.

Anodic passivation of iron

The impedance shown in Figure 3a displays the negative resistance and the characteristic associated loop visualizing the relaxation of the degree of passivity with the *a.c.* potential. Figure 3b shows the DLCFR. It exhibits a semi-circular shape located in the third quadrant of the Nyquist plane (negative real part, positive imaginary part), with the same characteristic frequency as the admittance. It can be concluded, that in the case of a passivation process the capacitance decreases with increasing amount of passivating material. The static derivative $\Delta C_\Omega(0)/\Delta E_\omega$ = 600 μF V^{-1} cm^{-2} extracted from Figure 3b matches reasonably well the value corresponding to the annihilation, over the effective passivation range, (about 0.1V), of the double layer, (60 μF cm^{-2}), by a dielectric oxide layer of much lower capacitance.
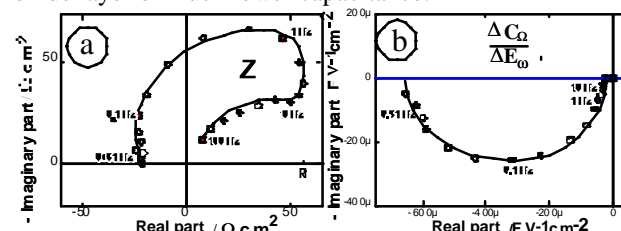

Figure 3 : Anodic passivation of iron in sulfate medium. Vicinity of the Flade potential. pH=3.04,
E=-0.323V/ESS, j=1.79 mA cm^{-2}. Complex plane plots of -a.Impedance.–b.DLCFR: $\Delta C_\Omega(\omega)/\Delta E_\omega$, Frequency in Hz.

For all the systems investigated it was found that the double layer capacitance exhibits a frequency response with the same time-constants as the faradaic current flowing at the interface. The emphasis is put on the interpretation of DLCFR in terms of relaxation of the interface configuration predicted by available models.

3. References

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